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                MINERALOGICAL APPLICATIONS OF HIGH-TEMPERATURE REACTION CALORIM--ETC(U)
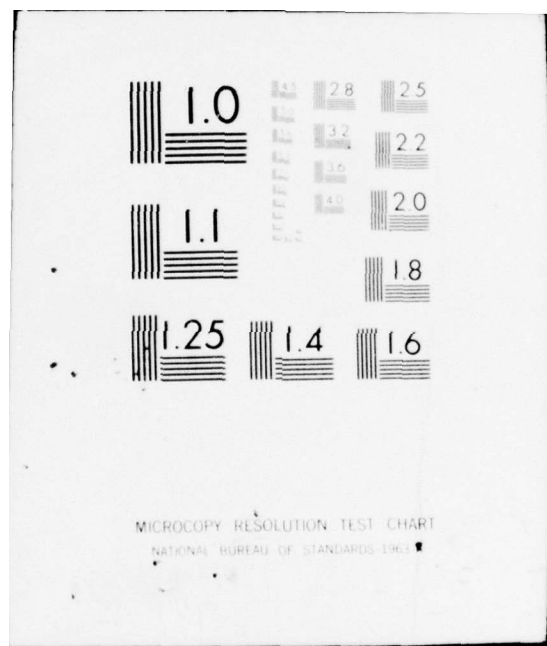   1976   O J KLEPPA   DAHC04-74-G-0009

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Mineralogical Applications of High-Temperature Reaction Calorimetry

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INTRODUCTION

Mineralogical applications of reaction calorimetry may involve either
(a) *direct combination and transformation studies*, or (b) *solution calorimetry*.
Among these approaches the latter is the more generally useful. While solution
calorimetry using acid solvents at or near room temperature has proved useful
in some cases, it has very serious limitations when the minerals involved are
dense and refractory. This is the principal domain of high-temperature solution
calorimetry and of the modern heat flux calorimeter.

One of the crucial problems in high-temperature solution calorimetry is
the choice of a suitable solvent, and some criteria used in the selection of oxide
melt solvents for work on refractory minerals are outlined. Examples of applica-
tions of reaction calorimetry to mineral systems include studies of (a) enthalpies
of formation from component oxides, (b) phase transformations, (c) disorder
problems, and (d) mineralogical reactions and equilibria.

For reacting system at fixed composition or for a simple, first order phase
transformation, we have the well-known thermodynamic relation

$$\Delta G_T = \Delta G_T^0 + \int_1^{P_{eq}} \Delta V_T dP$$

$$= \Delta H_T^0 - T \Delta S_T^0 + \int_1^{P_{eq}} \Delta V_T dP \tag{1}$$

At equilibrium $\Delta G_T = 0$. Thus we have also

$$\int_1^{P_{eq}} \Delta V_T dP = - \Delta G_T^0 \tag{2}$$

In these expressions, ΔG_T^0 is the standard Gibbs energy change at temperature
T, ΔH_T^0 is the standard enthalpy and ΔS_T^0 is the standard entropy change;

ΔV_T is the volume change associated with the reaction. Due to compressibility ΔV_T will, in general, be different from ΔV_T^0 the volume change at one atmosphere pressure. However, as long as we are dealing with condensed phases and moderate pressures, we have

$$\Delta V_T \approx \Delta V_T^0$$

and

$$P_{eq} \simeq -\frac{\Delta G_T^0}{\Delta V_T^0} \tag{3}$$

Thus, if ΔG_T^0 and ΔV_T are known, P_{eq} may be calculated or estimated.
The Clapeyron equation

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta S}{\Delta V} \simeq \frac{\Delta S^0}{\Delta V^0} \tag{4}$$

similarly provides a link between the temperature derivative of the equilibrium pressure and the change in entropy.

The implication of these relationships is clear. If we have information on ΔH^0, ΔS^0, and ΔV^0 for a given reaction or phase transformation, i.e. if we have thermodynamic data valid at one atmosphere pressure, we can readily estimate the pressure–temperature equilibrium curve. If we also know ΔV as a function of temperature and pressure, we can obtain more precise values.

Our principal interest in the present paper will be focused on the purely thermal quantities ΔS^0 and ΔH^0. For completely ordered phases S^0 and ΔS^0 in principle may be derived from low temperature heat capacity data, via the third law
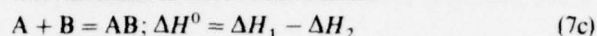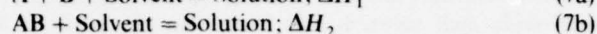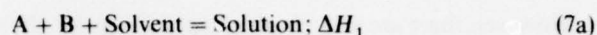
$$S^0 = \int_0^T C_P d\ln T \tag{6}$$

Where the relevant heat capacity data are lacking, approximate values of S^0 for condensed phases at high temperatures often can be estimated. However, complications arise where the substances involved are disordered. Under these circumstances configurational entropies sometimes can be estimated from detailed structural information.

It is more difficult to make realistic predictions or estimates of ΔH^0, which usually must be obtained from data based on reaction calorimetry.

SOLUTION CALORIMETRY OF MINERALS

In the years immediately following World War II, considerable progress was made in the general area of mineral thermochemistry. This progress was sparked by the development by Torgeson and Sahama (1948) of precision hydrofluoric acid solution calorimetry. The thermodynamic basis of this method is very straightforward:

$$A + B + \text{Solvent} = \text{Solution}; \Delta H_1 \qquad (7a)$$
$$AB + \text{Solvent} = \text{Solution}; \Delta H_2 \qquad (7b)$$

$$A + B = AB; \Delta H^0 = \Delta H_1 - \Delta H_2 \qquad (7c)$$

Thus the standard enthalpy change for a given reaction (here $A + B = AB$) may be obtained from the difference between two measured enthalpies of solution. Following the work of Torgeson and Sahama, hydrofluoric acid solution calorimetry was adopted by a number of investigators in the silicate field, notably in studies of feldspars by Kelley *et al.* (1953), Kracek and Neuvonen (1952), and others. More recent work based on this method has been carried out, e.g. by Waldbaum (1966).

It is believed that the first purely thermochemical calculation of the P–T curve for an important silicate equilibrium was that of Kracek, Neuvonen and Burley (1951) on the stability of jadeite. This work preceded by several years the experimental equilibrium work of Robertson, Birch and MacDonald (1957), and of Birch and Le Conte (1960). While the agreement between the calculated and the experimental values was far from perfect, these studies served to illustrate both the potential of the thermochemical approach, and also some of its obvious limitations. Thus, Kracek, Neuvonen and Burley found that jadeite, as most other dense minerals, dissolves only with considerable difficulty in hydrofluoric acid, even at 75 °C. Their results also indicated that the observed enthalpies of solution to some extent reflected the past treatment of the jadeite samples, i.e. whether the jadeite powders had been ground in an agate or a mullite mortar. Another problem, which is common to all work on hydrofluoric acid solution calorimetry, is the fact that the observed enthalpies of solution are large numerical quantities compared to the enthalpy changes in typical mineral reactions and phase transformations. As a result of these various problems it soon became recognized that HF solution calorimetry, although clearly useful for certain types of mineral equilibrium studies, has a somewhat limited range of application. A new and more powerful approach was provided by oxide melt solution calorimetry.

In this method, which originated with the work of Yokokawa and Kleppa (1964, 1965), the aqueous acid solvent of conventional, room temperature solution calorimetry, is replaced by a high-temperature oxide melt solvent. The technique has certain obvious advantages compared to the room temperature methods:

(1) It allows thermochemical study of a wider range of oxidic substances, and, particularly of dense and refractory minerals.

(2) The observed enthalpies of solution are numerically much smaller than in acid solution work. Without loss in the precision of the *enthalpies of reaction* this permits the use of heat flux calorimetry.

(3) It is possible to work with much smaller samples than in conventional acid solution calorimetry. With samples of the order of 25 mg, it is feasible to combine solution calorimetry with high pressure-high temperature synthesis and equilibrium work.

However, there are also disadvantages. For example, it is not convenient to use oxide melt solution calorimetry for the study of the hydrous minerals which frequently participate in low-grade metamorphic reactions.

REACTION CALORIMETRY AT HIGH TEMPERATURE

Two basically different ideas have provided the basis for design of calorimeters operated at high temperature. The idea behind the *adiabatic* and 'conventional' (or quasi-adiabatic) designs has been to reduce as far as possible (ideally to eliminate) the heat flux ('heat leak') between the calorimeter and the surroundings.

There are several different circumstances which tend to limit the effectiveness both of adiabatic and quasi-adiabatic calorimeters at high temperature. The most serious undoubtedly are related to the increasing importance of radiation in heat transfer as the temperature is increased.

In the design of *heat flux* calorimeters no attempt is made to reduce the heat leak. Instead one tries to fix the design parameters in such a way that the integrated heat flux can be measured reproducibly and conveniently. Figure 1 illustrates typical time temperature curves for adiabatic, conventional and heat flux calorimeters. In our own work we have found it convenient to design our heat flux calorimeters in such a way that the time constant of the calorimeter is of the order of 3 minutes. Under these conditions a temperature change which occurs in the calorimeter at time 0, will have decayed to less than 1/1000
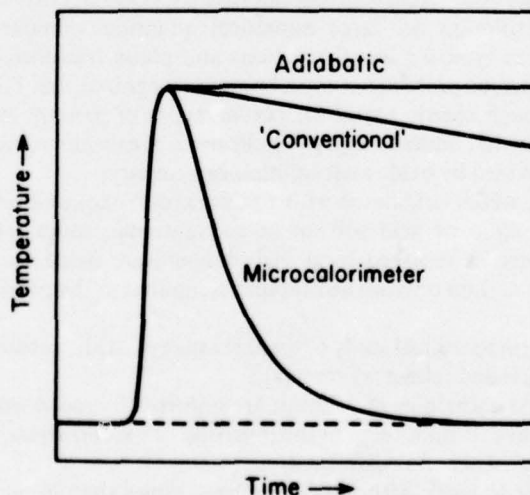

Figure 1. Schematic time–temperature curves for adiabatic, conventional (i.e. 'quasi-adiabatic') and micro (i.e. 'heat flux') calorimeters.

of its maximum value in about one-half hour. This usually is a convenient time scale for solution calorimetry.

Under favourable circumstances (for each) the heat flux calorimeter cannot compete with the adiabatic calorimeter with respect to experimental precision. In fact, we have found it very difficult to achieve a precision better than about $\pm$ 0.5 per cent in heat flux calorimetry carried out at any temperature. However, while the difficulties associated with adiabatic and conventional calorimetry increase dramatically with temperature, those of heat flux calorimetry increase much more slowly. Also, what heat flux calorimetry may lose in precision, it may regain in simplicity, convenience and reliability.

In solution (as distinct from bomb) calorimetry, the calorimetric process usually is not instantaneous, but may require a significant period of time. In order to monitor the progress of the dissolution of the solid sample, and the
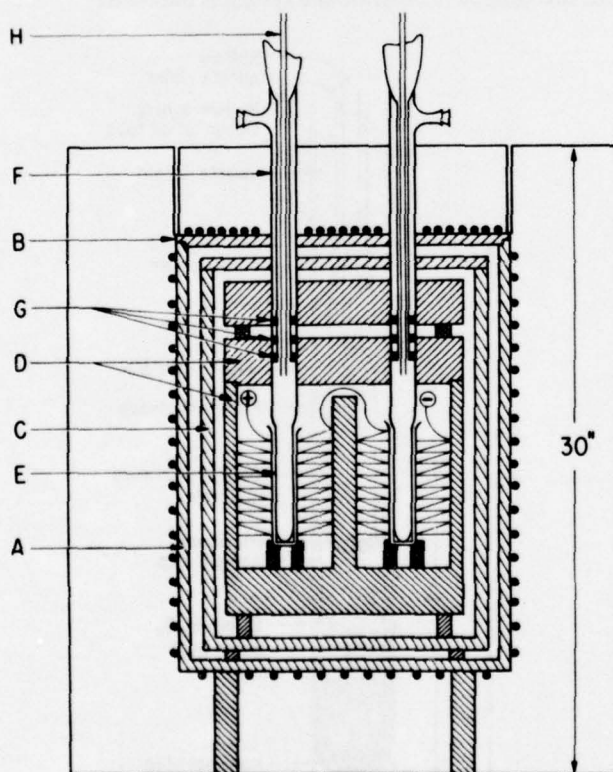
Figure 2. Schematic diagram of Calvet-type twin microcalorimeter for temperature up to about 800 °C. A: Main heater; B: Top heater; C: Heavy shield; D: Nickel block; E: Calorimeter; F: Protection tube; G: Radiation shields; H: Manipulation tube; + — − : Thermopile.

completion of the dissolution process, it is desirable to use a heat flux calorimeter with very good baseline stability. Such an apparatus is, e.g. the Calvet-type twin micro-calorimeter shown in Figure 2 (Kleppa, 1960). The twin construction, with two essentially identical calorimeters and thermopiles connected in series but backed against each other, is particularly useful in reducing the need for very close temperature control. This can be a very difficult problem at high temperatures. The apparatus illustrated in Figure 2 has a calorimeter block ('thermostat') constructed from pure nickel, which is a suitable material for operation in air at temperatures up to 7–800 °C. By choosing other construction materials such as inconel, stainless steel, nichrome, Kanthal, or aluminium oxide, the upper temperature limit of the apparatus may be increased to that indicated for the chosen material. As the temperature of operation is raised, problems frequently arise in connection with electrical noise in the thermopile system. Careful shielding of the thermopile system is indicated.
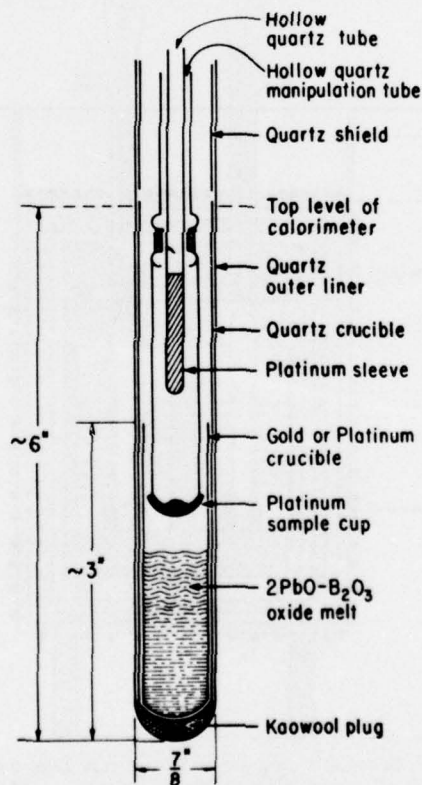

Figure 3. Schematic diagram of experimental arrangement used in oxide melt solution calorimetry.

Various experimental arrangements have been tried within the calorimeter proper. Our own preferred set-up is shown in Figure 3. Prior to the solution experiment the powdered sample (150–250 mesh; ~ 25 mg) is held in a shallow platinum cup above the surface of the solvent. Dissolution of the sample is initiated by dipping the cup into the melt. Stirring is manual by moving the platinum cup up and down several times.

Oxide Melt Solvents

In their initial work, Yokokawa and Kleppa (1964, 1965) explored the potential of liquid vanadium pentoxide at a calorimetric solvent at 700 °C. The results of this early exploration are summarized in Figure 4, which gives the
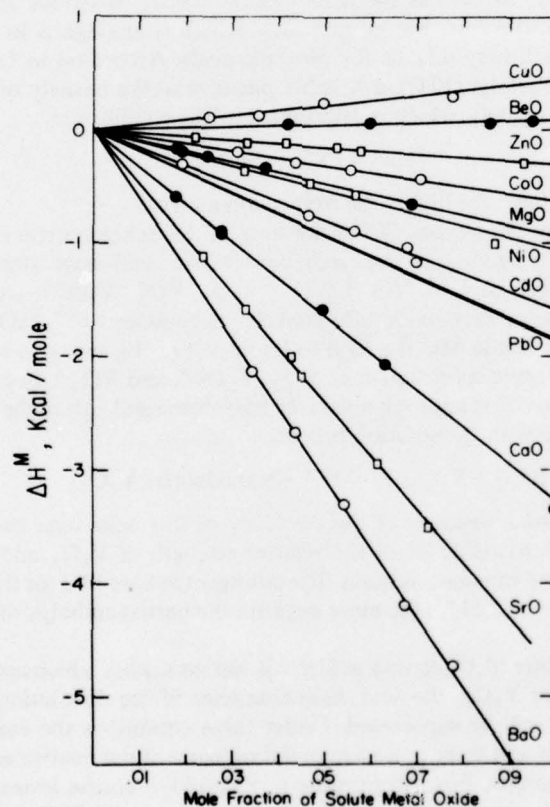

Figure 4. Molar integral enthalpies of mixing of liquid V_2O_5 + solid oxides at about 700 °C (Reprinted with permission from T. Yokkoawa and O. J. Kleppa, *Inorg. Chem.*, **4**, 1806 (1965). *Copyright by the American Chemical Society*).

enthalpy changes associated with the solution of some simple oxides MO in V_2O_5. Note in particular that for the oxides of the alkaline earth metals the enthalpies of solution change systematically in the sequence

$$BeO > MgO > CaO > SrO > BaO$$

with small positive values for BeO and quite large negative values for BaO. This is of course the order of increasing ionic radius of the cation and of increasing basicity of the solute oxide, which is consistent with the fact that the solvent V_2O_5 is a very strongly acidic oxide. These early results immediately suggest that an understanding of the elements of acid–base chemistry of melts is essential in any meaningful discussion of possible solvents for oxide melt solution calorimetry.

It is convenient to discuss the acid–base character of oxides and oxidic melts in terms of the Lux–Flood approach, which is analogous to the well-known Brönsted–Lowry scheme for protonic acids. According to Lux (1939) and Flood and Førland (1947), a suitable measure of the basicity of the melt is the oxygen ion activity, which is determined by the equilibrium

$$Acid + O^{-2} = Base.$$

The stronger the base, the higher the oxygen ion activity.

For the vanadium (V)-oxygen system we may in this scheme write a series of possible (but not necessarily realized) consecutive acid–base steps, which involve species such as V^{+5}, VO^{+3}, VO_2^+, V_2O_5, VO_3^-, $V_2O_7^{-4}$, and VO_4^{-3}. Similarly we may for each oxide MO consider the species M^{+2}, MO, MO_2^{-2}, etc. When a basic solute MO is added to liquid V_2O_5, this will give rise to the formation of vanadate species such as VO_3^-, $V_2O_7^{-4}$, and VO_4^{-3} (or polymeric forms of these). To a first approximation the magnitude and sign of the enthalpy change associated with the solution process

$$MO(s) + V_2O_5(l) = M^{+2} + Vanadate~(in~V_2O_5)$$
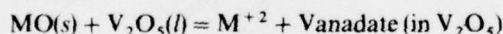
may be considered a measure of the tendency of this acid–base reaction to proceed from left to right, i.e. of the relative strength of V_2O_5 and M^{+2} as acids or of MO and vanadate as bases. The stronger the base MO (or the weaker the corresponding acid M^{+2}) the more negative the partial enthalpy of solution (ΔH_{MO}).

If the solute oxide M_nO_m is very acidic, e.g. has an acidity which approaches that of the solvent V_2O_5, the acid–base character of the dissolution process in large measure will be suppressed. Under these conditions the enthalpy of solution no longer will serve as a meaningful measure of the relative acid–base strengths of the solutes. For this purpose one should of course instead use an oxidic solvent of basic character, such as, for example, liquid PbO.

The vanadate–V_2O_5 mixtures which result from the dissolution of basic oxides in V_2O_5 are examples of buffered acid–base melts. Since most mixed oxide compounds contain two or more components of different acidity, it usually will be most convenient to use buffered melts as calorimetric solvent.

This also has the practical advantage that in the buffered regions the enthalpies of solution of acidic or basic oxides tend to vary less with composition.

We shall illustrate these problems further by considering the binary liquid system $PbO–B_2O_3$. At 700–800 °C, which is a convenient temperature for oxide melt solution calorimetry, the liquid range in this system extends from about 15 to 100 per cent B_2O_3 (Geller and Bunting, 1937). However, there is a miscibility gap in the high B_2O_3 region, which is also characterized by a very high viscosity. The system is glassforming, which has proved an advantage in checking that oxide samples do in fact go into solution.

Holm and Kleppa (1967) published the results of a calorimetric investigation of this system carried out at 800 °C. In this work the partial enthalpies of
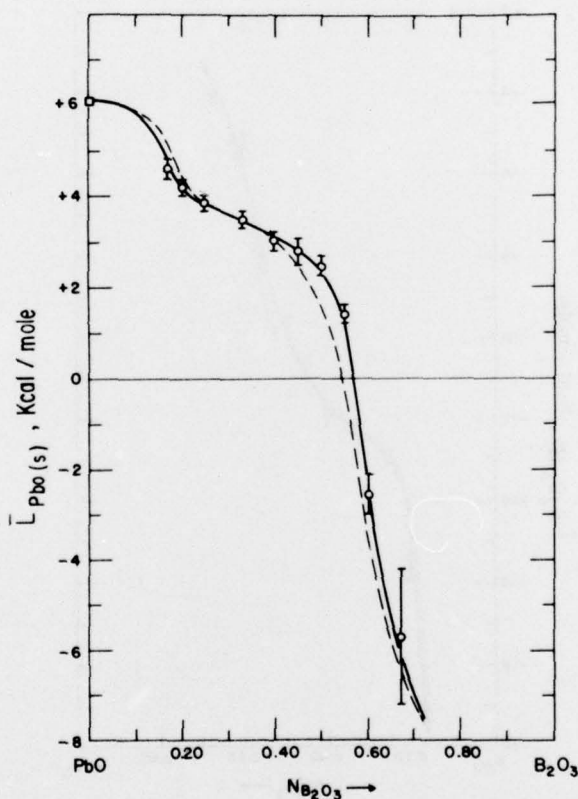

Figure 5. Partial mola-enthalpies of solid PbO in $PbO–B_2O_3$ melts at 800 °C □ Rodigina, Gomel'skii, and Luginina (1961); – – – By Gibbs–Duhem integration from $L_{B_2O_3}$. (Reprinted with permission from J. L. Holm and O. J. Kleppa, *Inorg. Chem.*, 6, 645 (1967). Copyright by the American Chemical Society).

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solution (actually $\Delta H/\Delta n$) of PbO(s) and B_2O_3(l) were measured at compositions between about 17 mole per cent and about 67 mole per cent B_2O_3. At higher B_2O_3 contents the melts were too viscous to allow precise calorimetry by the direct mixing approach.

The results reported by Holm and Kleppa are shown in Figures 5 and 6. Since the partial enthalpies of both components were measured, it was possible to check the internal consistency of the result by means of the Gibbs–Duhem equation. The results of this check are indicated as broken lines in the figures. On the whole there is reasonable agreement between the calculated and measured data.

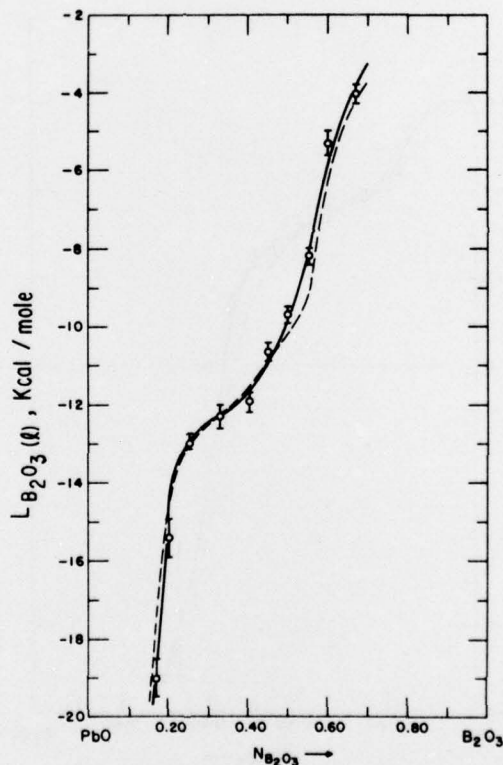The data suggest interesting changes in the acidity of the melt as the composi-

Figure 6. Partial molar enthalpies of liquid B_2O_3 in PbO–B_2O_3 melts at 800 °C -----By Gibbs–Duhem integration from $\bar{L}_{PbO}$. (Reprinted with permission from J. L. Holm and O. J. Kleppa, *Inorg. Chem.*, **6**, 645 (1967). Copyright by the American Chemical Society).

tion varies from basic in the high PbO region to acidic in the high B_2O_3 range. We interpreted the results to indicate that the liquid lead borate system contains at least two complex borate anions, which have oxygen–boron ratios of about 3.5–4.0 and 1.84–1.91, respectively. These ratios were obtained by attempting to locate the two steeply rising parts of the partial enthalpy versus composition curves. Between these two compositions the curves are flatter, which presumably reflects the presence of both of the two borate anions in comparable amounts, i.e. a buffer region. Most of our early calorimetric work was based on the use of melts with a $MO:B_2O_3$ ratio of 3:1. However, as a result of the work by Holm and Kleppa we now prefer a somewhat more acid melt with a ratio of 2:1.

Mineralogical Applications

The mineralogical applications of high temperature reaction calorimetry fall into the following main but related categories: (a) enthalpies of formation of refractory mixed oxides, (b) phase transformations, (c) disorder problems, and (d) mineralogical reactions and equilibria.

(a) Enthalpies of Formation

The thermodynamics of formation of refractory mixed oxides from its component oxides is not easily studied experimentally since this area is almost inaccessible to conventional room temperature calorimetric methods. During
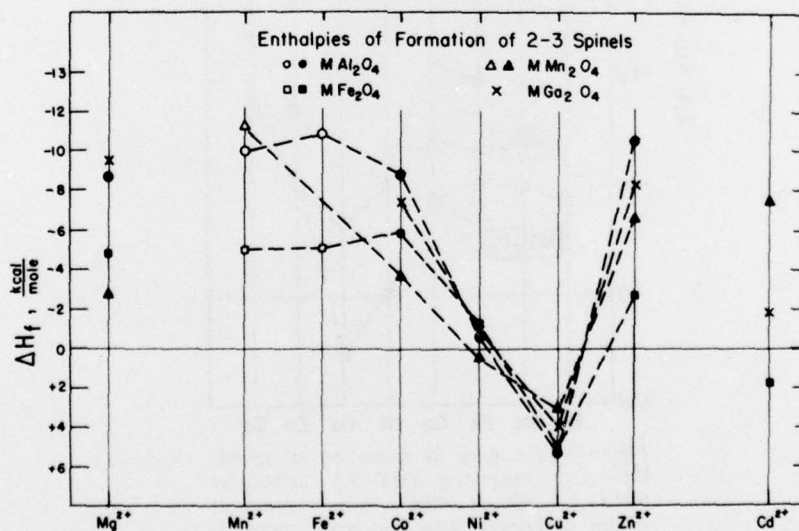

Figure 7. Enthalpies formation of 2–3 spinels from component oxides (Reprinted with permission from A. Navrotsky and O. J. Kleppa, *J. Inorg. Nucl. Chem.*, **30**, 479 (1968) Pergamon Press Ltd.)

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the past 10–15 years some progress has been achieved through solid–gas equilibrium methods, and in particular by means of the solid oxide electrochemical cells introduced by Kiukkola and Wagner (1957). However, as is so commonly the case, while work of this type may provide reliable data on the Gibbs energy of formation, it generally does not allow an unambiguous separation of ΔG_f into its appropriate enthalpy and entropy components. Oxide melt solution calorimetry has represented a new 'handle' on this problem. A particularly significant example is the investigation by Navrotsky and Kleppa (1968) of the thermodynamics of spinel formation, from which we take Figure 7, which gives enthalpy of formation data for a series of refractory 2–3 spinels
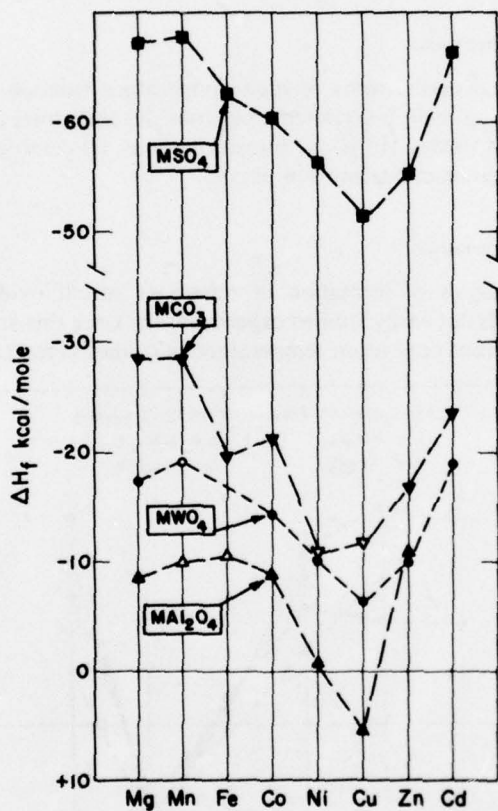

Figure 8. Enthalpies of formation of spinels (MAl_2O_4), tungstates (MWO_4), carbonates (MCO_3), sulphates (MSO_4) from component oxides (Reprinted with permission from A. Navrotsky and O. J. Kleppa, *Inorg. Chem.*, 8, 756 (1969). Copyright by the American Chemical Society).

taken from the families MAl_2O_4, MGa_2O_4, MMn_2O_4, and MFe_2O_4. More recently this work was extended by Müller and Kleppa (1973) to the corresponding compounds MCr_2O_4, which were studied by solution calorimetry at 900 °C. The systematic variation of ΔH_f with the cation is of considerable interest. However, Figure 8 which gives the enthalpies of formation of the compounds MAl_2O_4 compared with corresponding data for MWO_4, MCO_3, and MSO_4 shows that this variation with cation is nothing specific. The generally parallel character of the curves is apparent. The shift in ΔH_f to more negative values in the series

$$MAl_2O_4 < MWO_4 < MCO_3 < MSO_4,$$
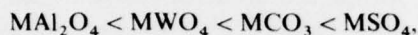
simply reflects the increasing acidity of the second oxide in the sequence
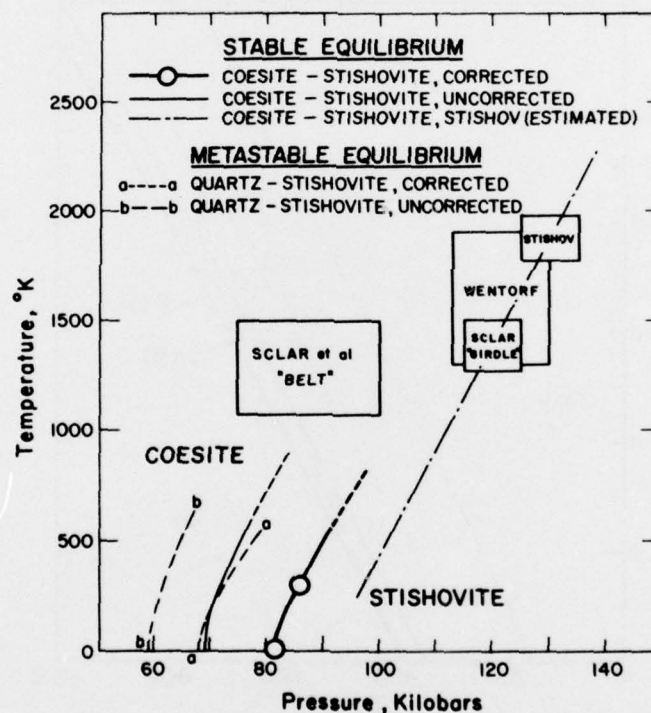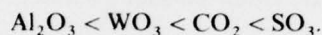
$$Al_2O_3 < WO_3 < CO_2 < SO_3.$$

Figure 9. P–T stability fields for the coesite-stishovite equilibrium and for the metastable equilibrium quartz-stishovite calculated from thermodynamic data Sclar *et al.* refers to Sclar, Young, Carrison, and Schwartz (1962); Wentorf refers to Wentorf (1962); Stishov refers to Stishov (1963). (Reprinted with permission from J. L. Holm, O. J. Kleppa and E. F. Westrum, *Geochim. Cosmochim. Acta*, **31**, 2289 (1967) Pergamon Press Ltd.)

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(b) Phase Transformations

It is frequently found that phase transformations in solid mineral systems are very sluggish, and that therefore equilibrium can be achieved in the laboratory only at quite high temperatures. For this reason quantitative equilibrium studies carried out *at temperature* may be very difficult and at times even impossible. However, there are no such restrictions on the thermodynamic calculations, which in principle will apply at any temperature.

Examples of important calculated phase equilibria in mineral systems are reported by Holm, Kleppa and Westrum (1967) in their work on the high pressure phases of silica. Figure 9 gives the thermodynamically calculated $P-T$ curve for coesite–stishovite, and for the quartz–stishovite transformation, along with some static equilibrium data for the former equilibrium.
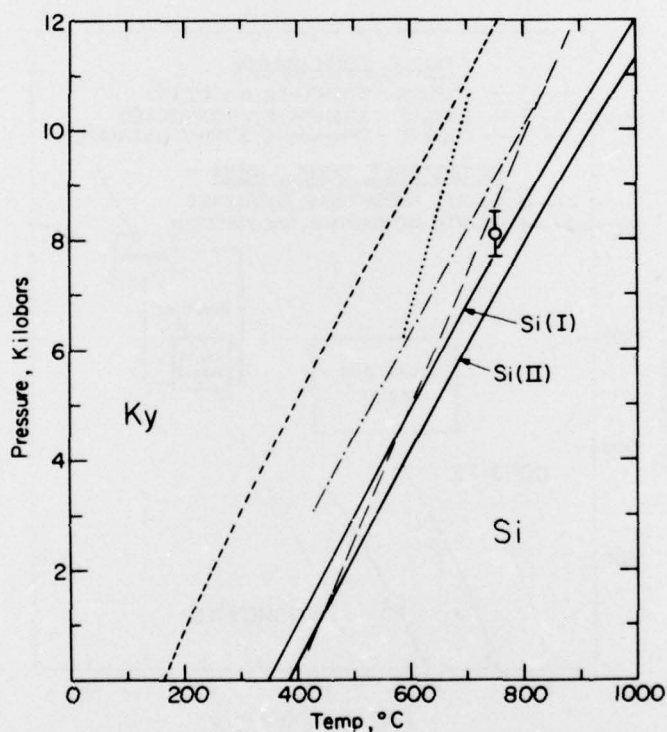

Figure 10. Comparison of calculated P–T curves for the kyanite–sillimanite equilibrium with some experimental curves. —————— Anderson and Kleppa (1969); – – – – Holm and Kleppa (1966); – · – · – · – Weill (1966); ——— ——— Richardson, Bell, and Gilbert (1968); . . . . . . Althaus (1967); ♂ Newton (1966). (Reproduced with permission from P. A. M. Anderson and O. J. Kleppa, *Amer. J. Sci.*, 267, 285 (1969).)

The thermochemical results for the quartz–stishovite transformation are of particular interest, since this equilibrium occurs in the stability field of coesite and cannot be studied by the usual static equilibrium methods. However, this transformation takes place in shock wave experiments (e.g. see, Davis, 1972).

Another phase transformation, which has been rather extensively studied by high temperature-high pressure methods, and for which good thermochemical data are available both on ΔH^0 and on ΔS^0, is the kyanite–sillimanite equilibrium. Figure 10 gives a summary of some of the P–T data for this transformation taken from Anderson and Kleppa (1969). Note that while there is now reasonable agreement between calculated and experimental equilibrium pressures, this agreement does not extend to the dP/dT slopes which are somewhat higher in the equilibrium experiments than in the calculations. There is now good reason to believe that this discrepancy is due to some Al–Si disorder in the sillimanite structure, which makes the entropy of sillimanite somewhat larger than given by the third law value (e.g. see, Holdaway, 1971).

(c) Disorder Problem

It has been recognized for some time that structural disorder is an important phenomenon in a number of mixed phases of refractory character such as, e.g. in the spinels, mullite, pyroxenes, feldspars. As an example, let us first consider the disordering problem in spinel, $Mg[Al]_2O_4$. At low temperature the equilibrium state of this mineral has all the magnesium ions located on the tetrahedral interstitial sites in the essentially close packed array of oxygen ions; similarly, the aluminium ions are located on octahedral sites. However, when this mineral is heated above 800 °C, a disordering transformation occurs which moves a fraction (x) of the magnesium ion to the octahedral sites and a corresponding number of aluminum ions to the tetrahedral sites (Hafner and Laves, 1961). The state of this partially disordered spinel may be described as

$$Mg_{1-x}Al_x[Al_{2-x}Mg_x]O_4.$$

Figure 11 gives a plot of the configurational entropy associated with disorder in a spinel, as a function of the disorder parameter x. Note in particular the very sharp (infinite slope) rise of the configurational entropy for small values of x. It is this sharp initial rise of the entropy with x which makes structural disorder a very general problem in refractory mixed oxides at high temperature.

To a first approximation it may be assumed that the enthalpy change associated with the disordering process in spinels is proportional to x, i.e.

$$\Delta H = x\Delta H_{int}, \tag{8}$$

where the interchange enthalpy, ΔH_{int}, is a constant characteristic of the considered spinel. If ΔS is equal to the configurational entropy

$$\Delta S = -R\left[x \ln x + (1-x)\ln(1-x) + x\ln\frac{x}{2} + (2-x)\ln\left(1-\frac{x}{2}\right)\right] \tag{9}$$

and we may set

$$S = -R \left([x \ln x + (1-x) \ln(1-x)] + 2\left[\frac{x}{2} \ln \frac{x}{2} + \left(1-\frac{x}{2}\right) \ln\left(1-\frac{x}{2}\right)\right] \right)$$
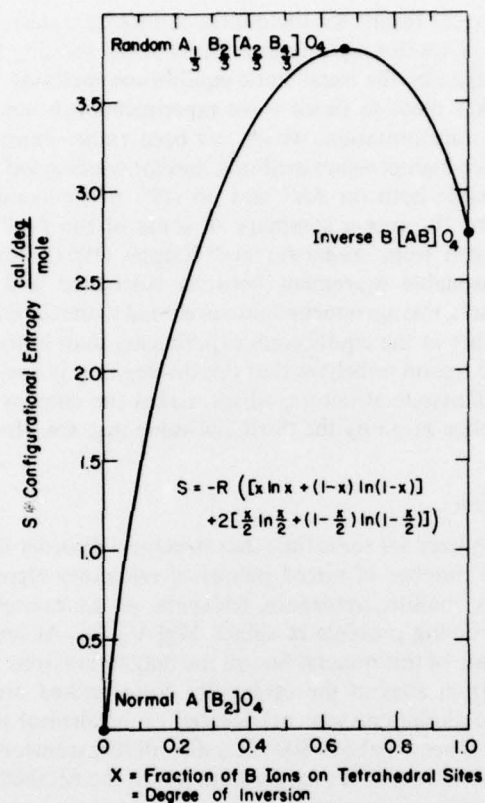
Figure 11. The dependence of the configurational entropy in spinels on the degree of inversion, x (Reprinted with permission from A. Navrotsky and O. J. Kleppa, *J. Inorg. Nucl. Chem.*, **29**, 2701 (1967) Pergamon Press Ltd.)

$$\Delta G = \Delta H - T \Delta S. \qquad (10)$$

By imposing the equilibrium requirement $d\Delta G/dx = 0$, we obtain

$$-\frac{\Delta H_{int}}{RT} = \ln \frac{x^2}{(1-x)(2-x)}, \qquad (11)$$

i.e. a relation between x, ΔH_{int}, and T. Navrotsky and Kleppa (1967) applied this model to $MgAl_2O_4$, and made a direct determination of ΔH for a natural spinel by means of oxide melt solution calorimetry. From these results and other information they concluded that for $MgAl_2O_4$ at 1000 °C, $\Delta H_{int} \approx 10$ kcal/mole and $x \approx 0.1$.

More recently a modified form of this simple disordering model was adopted by Holdaway (1971) in order to resolve some of the internal discrepancies between the experimental observations and the thermodynamic data for the kyanite–sillimanite–andalusite (Al_2SiO_5) system. Specifically, Holdaway assumes partial cation exchange between Al and Si atoms located on their respective tetrahedral sites in the sillimanite structure, according to the reaction

$$Al_{Al} + Si_{Si} = Si_{Al} + Al_{Si}. \tag{12}$$

His principal numerical input was his experimentally measured dP/dT slope of the sillimanite–andalusite phase boundary, which gave him an interchange enthalpy, ΔH_{int} of about 14.75 kcal/mole. With this interchange enthalpy, one would predict about 20 per cent disorder in sillimanite at 1400 °C.

Quite recently oxide melt heat of solution measurements on samples of natural sillimanite heat-treated at 1200–1700 °C at pressures of 16–23 kbar have been reported by Navrotsky, Newton, and Kleppa (1973). The results are shown in Figure 12 and indicate a distinct enthalpy of solution decrement relative to unheated sillimanite of about 1.3 kcal/mole by samples run at 1400–1550 °C. Analysis of these results in terms of the mentioned disordering model yields a value of $\Delta H_{int} = 16 \pm 1$ kcal/mole, in good agreement with Holdaway's value derived on entirely different grounds. At temperatures above 1550 °C, larger heat of solution decrements were observed. It is possible that these are due to some unknown and even more profound disordering process.
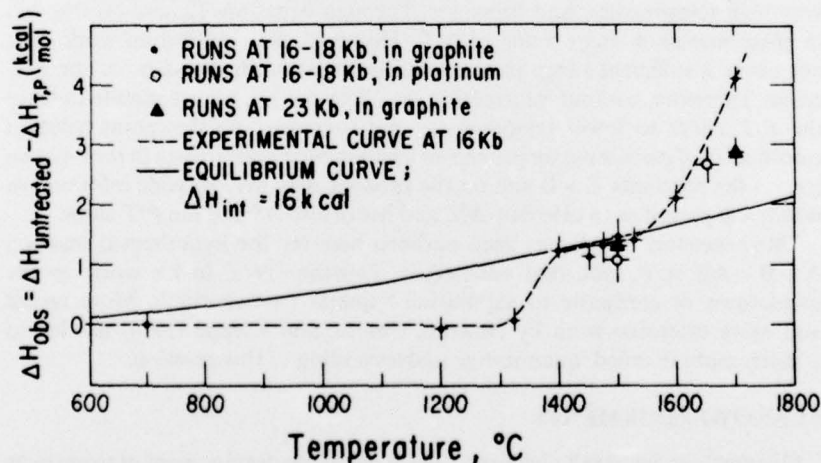

Figure 12. Heat of solution data on quenched samples of sillimanite heat-treated at high pressure. Solid line is calculated from simple Al–Si tetrahedral disorder (Eq. (12)) with $\Delta H_{int} = 16$ kcal/mole (Reprinted with permission from A. Navrotsky, R. C. Newton and O. J. Kleppa, *Geochim. Cosmochim. Acta*, 37, 2497 (1973) Pergamon Press Ltd.)

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(d) *Mineralogical Reactions and Equilibria*

The discussion above has focused on only one of the serious problems associated with the application of thermochemical methods to mineral reactions and equilibria, i.e. the problem of structural disorder. Another problem, which we have not discussed, has to do with the effect of chemical impurities. For example, if we have thermodynamic data for pure, ordered phases only, how do the results of a thermodynamic calculation apply to a real system in which significant amounts of impurities as well as structural disorder may be present? Along the same line of reasoning, what will be the influence on the considered equilibrium of more extensive solid solution formation or deviation from stoichiometry, which at times may vary significantly with changes in temperature and pressure? While it is possible to give partial and qualitative answers to some of these questions on the basis of chemical knowledge and physical intuition, more quantitative answers generally will require detailed thermodynamic information on the phases which actually participate in the considered reaction. As an example let us consider the hypothetical reaction

$$A + B = AB.$$
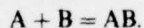
If carried out in the laboratory, this reaction may well be associated with solid solubility of **A** in **B** and of **B** in **A**, various impurities in both **A**, **B** and **AB**, and perhaps some structural disorder and solid solubility in the compound **AB**. Since the extent of these effects may be unknown or difficult to assess, it may be very difficult to make a realistic quantitative prediction about the equilibrium.

Let us assume that this reaction is very sluggish and can be studied only at very high temperatures and pressures. Through equations (2) and (3) this will in effect furnish a single value of ΔG^0. However, the equilibrium work does not cover a sufficient range in temperature to establish the slope of the P/T curve. Therefore, without information on ΔS or on ΔH, we are unable to trace the P/T curve to lower temperatures and pressures. At this point solution calorimetry, *if carried out on the phases which actually participate in the reaction* (i.e. on the reactants $A + B$ and on the product **AB**), may provide information which will permit us to calculate ΔH, and hence also ΔS and the P/T slope.

The procedure which has been outlined here for the hypothetical reaction $A + B = AB$ is, in fact, that adopted by Newton (1972) in his work on the breakdown of cordierite to sapphirine + quartz (+ enstatite?). More recent and more extensive work by Newton, Charlu, and Kleppa (1974) has led to a much more detailed, quantitative understanding of this reaction.

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REFERENCES

Althaus, E. (1967), *Contr. Mineralogy and Petrology*, **16**, 29–44.

Anderson, P. A. M. and O. J. Kleppa (1969), *Am. J. Sci.*, **267**, 285–290.

Birch, F. and P. LeConte (1960), *Am. J. Sci.*, **258**, 209–217.

Davies, G. F. (1972), *J. Geophys. Res.*, **77**, 4920–4933.

Flood, H. and T. Førland (1947), *Acta Chem. Scand.*, **1**, 592–604.

Geller, R. F. and E. N. Bunting (1937), *J. Res. Natl. Bur. Stds.*, **18**, 585–593.

Hafner, S. and F. Laves (1961), *Z. Krist. Min.*, **115**, 321–330.

Holdaway, M. J. (1971), *Am. J. Sci.*, **271**, 97–131.

Holm, J. L. and O. J. Kleppa (1966), *Amer. Mineral.*, **51**, 1608–1616.

Holm, J. L. and O. J. Kleppa (1967), *Inorg. Chem.*, **6**, 645–648.

Holm, J. L., O. J. Kleppa and E. F. Westrum (1967), *Geochim. Cosmochim. Acta*, **31**, 2289–2307.

Kelley, K. K., S. S. Todd, R. L. Orr, E. G. King and K. R. Bonnickson (1953), *U. S. Bur. Mines Rept. Inv.*, 4955.

Kiukkola, K. and C. Wagner (1957), *J. Electrochem. Soc.*, **104**, 308–316.

Kleppa, O. J. (1960), *J. Phys. Chem.*, **64**, 1937–1940.

Kracek, F. C. and K. J. Neuvonen (1952), *Am. J. Sci.*, Bowen Vol., 293–318.

Kracek, F. C., K. J. Neuvonen and G. Burley (1951), *Washington Acad. Sci. J.*, **41**, 373–383.

Lux, H. (1939), *Z. Elektrochem.* **45**, 303–309.

Muller, F. and O. J. Kleppa (1973), *J. Inorg. Nucl. Chem.*, **35**, 2673–2678.

Navrotsky, A. and O. J. Kleppa (1967), *J. Inorg. Nucl. Chem.*, **29**, 2701–2714.

Navrotsky, A. and O. J. Kleppa (1968), *J. Inorg. Nucl. Chem.*, **30**, 479–498.

Navrotsky, A. and O. J. Kleppa (1969), *Inorg. Chem.*, **8**, 756–758.

Navrotsky, A., R. C. Newton and O. J. Kleppa (1973), *Geochim. Cosmochim. Acta*, **37**, 2497–2508.

Newton, R. C. (1966), *Science*, **151**, 1222–1225.

Newton, R. C. (1972), *J. Geol.*, **80**, 398–420.

Newton, R. C., T. V. Charlu and O. J. Kleppa (1974), *Contr. Mineral. Petrol.*, **44**, 295–312.

Richardson, S. W., P. M. Bell, and M. C. Gilbert (1968), *Am. J. Sci.*, **266**, 513–541.

Robertson, E. C., F. Birch and G. J. F. Macdonald (1957), *Am. J. Sci.*, **255**, 115–137.

Rodigina, E. N., K. Z. Gomel'skii, and V. F. Luginina (1961), *Russ. J. Phys. Chem.*, **35**, 884.

Sclar, C. B., A. P. Young, L. C. Carrison, and C. M. Schwartz (1962), *J. Geophys. Res.*, **67**, 4049–4052.

Stishov, S. M. (1963), *Doklady Akad. Nauk S.S.S.R.*, **148**, 1186–1188.

Torgeson, D. R. and TH. G. Sahama (1948), *J. Am. Chem. Soc.*, **70**, 2156–2160.

Waldbaum, D. R. (1966), *Ph.D. Thesis*, Harvard University, 247 pp.

Weill, D. F. (1966), *Geochim. Cosmochim. Acta*, **30**, 223–237.

Wentorf, R. H., Jr. (1962), *J. Geophys. Res.*, **67**, 3648.

Yokokawa, T. and O. J. Kleppa (1964), *Inorg. Chem.*, **3**, 954–957.

Yokokawa, T. and O. J. Kleppa (1965), *Inorg. Chem.*, **4**, 1806–1808.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Mineralogical applications of high-temperature calorimetry may involve either (a) direct combination and transformation work, or (b) solution calorimetry. Among these approaches the latter is the more generally useful.

A crucial problem in high-temperature solution calorimetry is the proper choice of a suitable solvent. Criteria used in the selection of oxide melt solvents for work on refractory minerals will be outlined.

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20. ABSTRACT CONTINUED

Examples of recent applications of reaction calorimetry to mineral systems will be given. These applications relate to studies of (a) phase transformations, (b) disordering processes, and (c) mineralogical reactions and equilibria.